REMARKS

Applicants respectfully request reconsideration of the present application in view of the foregoing amendments and in view of the reasons that follow.

Claim 1 is currently being amended to correct an informality. A detailed listing of all claims that are, or were, in the application, irrespective of whether the claims remain under examination in the application, is presented, with an appropriate defined status identifier. After amending the claims as set forth above, claims 1-10 and 12-15 are now pending in the application.

Applicants wish to thank the Examiner for withdrawing the previous rejection under 35 U.S.C. § 112.

Rejection of claims 1-2, 8-10, 12-13, and 14-15 based on Savale

Claims 1-2, 8-10, 12-13, and 14-15 were rejected under 35 U.S.C. § 102(e) as being anticipated by U.S. Patent No. 7,255,084 ("Savale").

In response, Applicants respectfully submit that Savale should be removed as prior art. Savale is a continuation of application No. PCT/EP2004/050340, filed on March 22, 2004. PCT/EP2004/050340 was published in English on October 14, 2004 and designated the U.S. Thus, Savale's § 102(e) date is March 22, 2004. The present application entered the National Stage on October 4, 2007 and claims priority under 35 U.S.C. § 120 to two PCT applications. One of the two PCT applications, PCT/EP2004/013676, has a filing date before the § 102(e) date of Savale of December 2, 2003. The claims of the present application find full support in PCT/EP2004/013676. Attached as Appendix A and Appendix B are published copies of PCT/EP2004/050340 and PCT/EP2004/013676 respectively. Accordingly, Applicants request that the rejection of claims 1-2, 8-10, 12-13, and 14-15 be withdrawn.

Rejection of claims 4-6 based on Savale

Claims 4-6 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Savale. As set forth above, Savale is not a proper prior art reference. Because Savale is not a proper prior art reference, independent claim 1 and its dependent claims 4-6 are allowable. Favorable reconsideration and withdrawal of the rejection based on Savale is respectfully requested.

Rejection of claims 3 and 7 based on Savale and Bekaert

Claims 3 and 7 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Savale in view of EP Patent No. 0856592 ("Bekaert"). As set forth above, Savale is not a proper prior art reference. Bekaert fails to cure the deficiencies of Savale. Because Savale is not a proper prior art reference and because Bekaert does not disclose the limitations of independent claim 1, claim 1 and its dependent claims 3 and 7 are allowable. Favorable reconsideration and withdrawal of the rejection based on Savale and Bekaert is respectfully requested.

Conclusion

Applicants believe that the present application is now in condition for allowance. Favorable reconsideration of the application as amended is respectfully requested.

The Examiner is invited to contact the undersigned by telephone if it is felt that a telephone interview would advance the prosecution of the present application.

The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by the credit card payment instructions in EFS-Web being incorrect or absent, resulting in a rejected or incorrect credit card transaction, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741. If any extensions of time are needed for timely acceptance of papers submitted herewith, Applicants hereby petition for such extension under 37 C.F.R. §1.136 and authorizes payment of any such extensions fees to Deposit Account No. 19-0741.

Respectfully submitted,

Date 9/3/2009

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Appendix A

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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Published:
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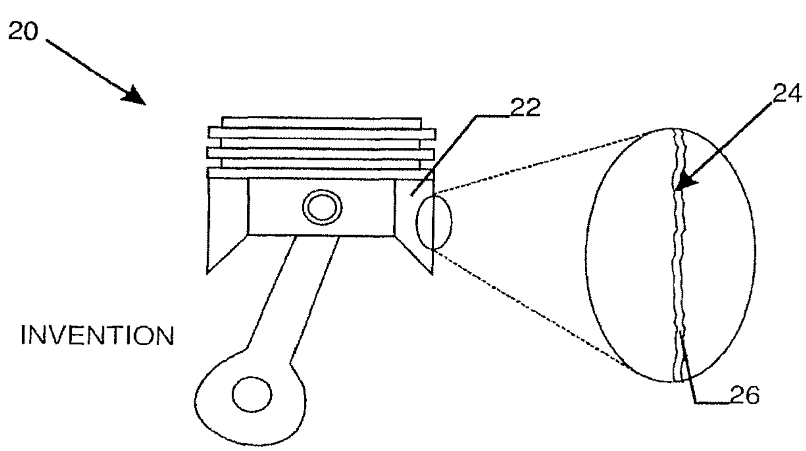
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** PISTON WITH A SKIRT HAVING A LOW COEFFICIENT OF FRICTION



(57) **Abstract:** A piston (20) for an internal combustion motor has a skirt (22) with a surface (24), which is at least partially polished and thereafter coated with a coating (26) having a hardness of greater than 8 GPa and having a coefficient of friction of less than 0.20. The piston has an increased performance, a longer lifetime and a reduced friction.

WO 2004/088113 A1

PISTON WITH A SKIRT HAVING A LOW COEFFICIENT OF FRICTION.

Field of the invention.

The present invention relates to a piston of an internal combustion motor, and more particularly to an improvement of the skirt surface of the piston. The invention also relates to a method of treating the skirt surface of the piston and to a use of the piston.

Background of the invention.

On the one hand, pistons are widely known and used in internal combustion motors. The motors often operate with a frequency of several thousands rotations per minute at elevated temperatures. A lot of attention has been given to the working of those pistons, and more particularly to the reduction of friction of the piston inside the cylinder bore. Incremental reductions in friction or incremental improvements in lubrication may increase substantially the efficiency of the motor.

On the other hand, coatings such as diamond-like coatings are well known in the art, amongst others, for their hardness, for their corrosion resistance and for their low coefficient of friction. Diamond-like coatings have been applied successfully on various automotive components such as valve heads, rods, shafts, piston rings, and cylinder heads...

Despite the widely spread use of pistons of internal combustion motors and despite the existence of hard coatings such as diamond-like coatings, application of hard coatings such as diamond-like coatings to the skirts of pistons has proved to be unsuccessful and not in line with other applications of diamond-like coatings.

Summary of the invention.

It is an object of the invention to avoid the disadvantages of the prior art.

It is a further object of the invention to reduce the friction of a working piston of an internal combustion motor.

It is another object of the invention to reduce the need for an additional lubricant.

It is still another object of the invention to increase the lifetime of a piston of an internal combustion motor.
It is yet another object of the invention to increase the performance of a piston of an internal combustion motor.

According to a first aspect of the present invention, there is provided a piston with a skirt. The skirt has a surface, which is at least partially polished and thereafter coated with a coating having a hardness of greater than 8 GPa and having a coefficient of friction of less than 0.20.
The term hardness refers to a Vickers hardness.
The terms coefficient of friction refer to a friction coefficient as measured in a ball on disk test in dry circumstances. Reference is here made to ASTM G99 and to DIN 50 324. The friction test can be performed by means of a multi-axis tribometer such as type TE 79 provided by Phoenix Tribology Ltd.

The part of the surface of the skirt is preferably polished until a surface with a flat surface morphology is obtained. The surface has at least partially a ten-point mean roughness Rz of less than 1.0.
The ten-point mean roughness is determined as follows. A section of standard length is sampled from the mean line on the roughness chart. The distance between the peaks and valleys of the sampled line is measured in the y-direction. Then the average peak is obtained amongst the five tallest peaks and the average valley is obtained amongst the five lowest valleys. The sum of these two values is then made and is expressed in micrometer (μm).

The part of the surface of the skirt is preferably polished until a surface roughness Ra of less than 0.15 has been reached.
The term Ra refers to the arithmetical mean roughness and its value is expressed in micrometer (μm). Preferably Ra ranges from 0.08 to 0.15, most preferably from 0.08 to 0.12, e.g. from 0.08 to 0.10.

The working of the invention can be explained as follows.

A prior art piston skirt is provided with striations, ridges or small grooves. Generally the skirt surface has a ten-point mean roughness Rz about 7 to 8 and an arithmetical mean roughness Ra ranging from about 1 to about 5. The reason is that the skirt surface must retain the lubricating oil in order to allow for the sliding while reducing wear and friction. The relatively high surface roughness of the skirt functions as a reservoir for the lubricant.
So the skirt surface has an image of relatively high peaks and deep valleys. Coating the skirt with a hard coating such as a diamond-like carbon coating will not take away the existing roughness. Only the peaks will be covered with a hard coating that will make contact with any neighboring part. The surface area of the peaks is too small to make any effect.
The present invention departs from the generally accepted assumption that the skirt surface must be rough. The invention provides a polishing treatment prior to the coating so that the landscape of the skirt surface is flattened and that more working surface becomes available so that the effect of diamond-like carbon coatings is more pronounced.
The polishing treatment reduces the existing roughness and the reservoir available for the lubricant. However, this has not been considered as a disadvantage due to the self-lubricating properties of diamond-like coatings and due to a reduced need for extra lubrication.

JP-A-2000-320670 discloses a surface treatment method for a piston of a hydraulic pump or a hydraulic motor. To improve the sliding performance of the piston in a bore a surface hardening treatment is applied, thereafter the hardened layer is polished and the polished layer is coated with diamond-like carbon. The working circumstances of a hydraulic pump or hydraulic motor, however, are not that severe as in an internal combustion motor.

According to the invention, preferably the hard coating is selected from the group of diamond-like carbon coatings, diamond-like nanocomposite coatings, and wolfram carbide coatings including any doped such coatings or a combination thereof.
The terms "wolfram carbide" coatings refers to wolfram carbide coatings as such but also to wolfram carbide coatings, which have been enriched with carbon or to WC/C coatings with an additional layer of carbon in order to reduce the friction.
For example, the hard coating may have two layers, a first layer of a diamond-like coating (DLC) and a surface layer of a diamond-like nanocomposite coating (DLN), which has a coefficient of friction, which is even lower than the coefficient of friction of DLC.
DLC coatings (a-C:H) are a mixture of sp2 and sp3 bonded carbon atoms with a hydrogen concentration between 0 - 80%.
DLN coatings (a-C:H/a-Si:O) are commercialized under the trademark DYLYN® and comprise C, H, Si and O:
a-Si:O enhances high temperature stability, leads to lower friction & lowers films stress
a-C:H provides diamond-like properties.

An intermediate tie layer may be present between the polished skirt surface and the coating in order to increase the adhesion between the substrate of steel or aluminum and the hard coating.
In case there is an intermediate tie layer, the intermediate tie layer may be selected from a group consisting of diamond-like nanocomposite coatings, doped diamond-like coatings, TiN coatings, Ti (C,N) coatings, i-C coatings, wolfram carbide coatings, SiN coatings, CrN coatings or a combination hereof.

The hard coating on the polished skirt surface may have a thickness ranging from 1 micrometer to 10 micrometer, for example from 2 micrometer to 6 micrometer, e.g. about 4 μm.

According to a second aspect of the invention, there is provided a method of treating a piston, where the piston has a skirt.

The method comprises the following steps:
a) polishing at least partially the surface of the skirt;
b) coating the thus polished surface with a coating having a hardness of greater than 8 GPa and having a coefficient of friction of less than 0.20.
Preferably the coating is done under vacuum, e.g. by means of a chemical vapor deposition (CVD) process, most preferably by means of a plasma assisted chemical vapor deposition (PACVD) process or by means of a mixed PVD/PACVD process.

The invention piston according to the first aspect of the invention or treated according to the second aspect of the invention may be used in an internal combustion engine.

Brief description of the drawings.
The invention will now be described into more detail with reference to the accompanying drawings wherein
FIGURE 1 shows a schematical drawing of a prior art embodiment of a piston;
FIGURE 2 shows a schematical drawing of a piston according to the first aspect of the invention.

Description of a prior art embodiment.
FIGURE 1 shows a prior art embodiment of a piston 10. The piston 10 has a skirt 12. An enlarged view of its surface 14 is also shown. This enlarged view shows a surface with roughnesses Ra ranging from 3 to 5 and even higher. The valleys between the peaks serve as reservoir for the lubricant and facilitate the mounting of the lubricant upwards. The coating of this prior art piston skirt with a hard coating does not lead to any substantial advantages. The reason is that any contact with e.g. the cylindrical bore is limited to the surfaces of the peaks, which are too small.

Description of the preferred embodiments of the invention.

Embodiment 1

FIGURE 2 shows an embodiment of a piston 20 according to the invention. The piston 20 has a skirt 22 which may be out of steel or out of aluminum or out of titanium. The skirt 22 has been subjected to a polishing treatment preferably until its surface 24 obtains a roughness Ra of below 0.10. Thereafter a PACVD process deposits a hard diamond-like carbon coating with a thickness ranging between 1 µm and 6 µm, a harness greater than 10 GPa and a coefficient of friction lower than 0.20.

The PACVD process mainly occurs as follows.

The pistons 20 with the polished skirt surfaces 24 are placed in a vacuum chamber.

A liquid organic precursor containing the elements C and H in suitable proportions is introduced in the vacuum chamber. A plasma is formed from the introduced precursor by an electron assisted DC-discharge using a filament with a filament current of 50-150 A, a negative filament bias DC voltage of 50-300 V and with a plasma current between 0.1 and 20 A and a composition is deposited on the piston skirt, to which a negative DC- bias or negative RF self-bias voltage of 200 to 1200 V is applied, in order to attract ions formed in the plasma.

The plasma generation and the vacuum deposition may be performed in one single chamber. The pistons 20 may be arranged on a rotatable support (in the upper part of the vacuum chamber) in a manner similar to that shown in US-patent 5,352,493. The base pressure in the vacuum chamber is 3x10-7 mbar and the typical working pressure is maintained at 1x10-4 to 1x10-3 mbar by diffusions pumps (controlled with throttle valves).

The piston skirts 22 can be cleaned by an in-situ (Ar-) plasma etching process prior to deposition. This plasma etching may last for 3 to

30 minutes. The piston skirt temperature does generally not exceed 200 °C during the deposition process. .

A liquid precursor is preferably preheated above 30 °C before or during release in the vacuum chamber. The precursor is delivered to the vacuum chamber e.g. through a heat resistant porous body with a porosity of e.g. 30 to 50 %. The precursor can continuously be metered in small quantities through a tube, which delivers it as a vapor or a mist to the porous body. Otherwise the precursor can be introduced in batch in an open reservoir, which is placed in the chamber before this is put to vacuum. This reservoir can be electrically heated prior to the start of the deposition process inside the chamber to form the vapor.

A bundle of alloyed Tungsten filaments is placed as a cathode typically at about -150 V (DC bias voltage) in front of the earthed porous body. The body itself, with the inlet tube for the precursor at the backside of the porous body may be mounted in the lower part of the chamber. The filament bundle is convexly bent, e.g. to a half circle in a vertical plane and with a length of 15 to 30 cm. The current in the cathode filaments is preferably between 50 and 120 A (AC). The plasma current (measured between filament bundle and earthed porous body) can then typically amount to about 0.5 to 3 A. Preheating the precursor may offer the advantage that the current needed afterwards in the cathode filaments (for generating the plasma) could be lowered.

The distance between the uppermost area of the bent cathode bundle and the piston skirt is at least about 20 cm. The deposition occurs from bottom to top through attraction of the plasma ions by the substrate support, which is put to a negative RF self-bias voltage of typically about 400 V. Also the RF frequency is preferably much lower than that used according to US patent 5,352,493; viz. between 100 and 500 kHz and specifically about 200 to 300 kHz.

Invention pistons for motors with two stroke cycles have shown an improved behavior with respect to existing prior art pistons. This improved behavior resulted from an increased lifetime or from an increased performance.

Embodiment 2

The following double coating has been deposited on a polished piston skirt 22:

- First a diamond-like carbon (DLC) coating of 3 µm;
- Thereafter, a diamond-like nanocomposite (DLN) coating of 1 µm in order to profit from the usually lower coefficient of friction of DLN (e.g. less than 0.10 for DLN instead of less than 0.20 for DLC). Although lower than the hardness of DLC, the DLN topcoat still has a hardness higher than 10 GPa.

Embodiment 3

First some tie layers have been deposited on a polished piston skirt, and thereafter an i-C coating has been deposited:

- a TiN layer;
- a Ti (C,N) layer;
- an i-C coating

The coating has a hardness of more than 30 GPa and the coefficient of friction is less than 0.10.

Embodiment 4

First a tie layer of a silicon-nitrogen doped diamond-like carbon coating is deposited on a polished piston skirt. This coating has a good adhesion to the substrate. Thereafter a DLC top layer is deposited.

Embodiment 5

First a tie layer of DLN is deposited as tie layer on the polished piston skirt. Thereafter a DLC top coating is deposited.

Embodiment 6

The initial rough surface of the piston skirt had following roughness parameters:

- Ra = 0.79 µm
- Rz = 6.32 µm

After polishing the piston skirt had a smooth planar surface with following roughness parameters:

- Ra = 0.02 µm
- Rz = 0.21 µm

The polished piston skirt has thereafter been covered with a DLC coating.

CLAIMS

1. A piston (20) for an internal combustion motor, said piston (20) comprising a skirt (22), characterized in that said skirt has a surface (24) which is at least partially polished and thereafter coated with a coating (26) having a hardness of greater than 8 GPa and having a coefficient of friction of less than 0.20.

2. A piston (20) according to claim 1, wherein said skirt (22) has a surface with a flat surface morphology and which has at least partially a ten-point mean roughness Rz of less than 1.0.

3. A piston (20) according to any one of the preceding claims, wherein said skirt (22) has a surface, which has at least partially an arithmetical mean roughness Ra of less than 0.15.

4. A piston (20) according to any one of the preceding claims wherein said coating (26) is selected from the group of diamond-like carbon coatings, diamond-like nanocomposite coatings, wolfram carbide coatings or a combination thereof.

5. A piston (20) according to any one of the preceding claims wherein an intermediate tie layer is present between said polished surface and said coating.

6. A piston (20) according to claim 5 wherein said intermediate tie layer is selected from a group consisting of diamond-like nanocomposite coatings, doped diamond-like coatings, doped diamond-like nanocomposite coatings, TiN coatings, Ti (C,N) coatings, SiN coatings, CrN coatings, wolfram carbide coatings or a combination hereof.

7. A piston according to any one of the preceding claims wherein said coating has a thickness ranging from 1 micrometer to 10 micrometer.

8. A method of treating a piston (20) of an internal combustion motor,
said piston having a skirt (22),
characterized in that said method comprises the following steps:
a) polishing at least partially the surface of said skirt (22);
b) coating said at least partially polished surface (24) with a coating (26) having a hardness of greater than 8 GPa and having a coefficient of friction of less than 0.20.

9. A method according to claim 8, wherein said coating is done in vacuum.

10. A method according to claim 8, wherein said coating is done by means of a CVD process, a PVD process, a PACVD process or a mixed PVD/PACVD process.

11. Use of a piston according to any one of claims 1 to 7 in an internal combustion motor.

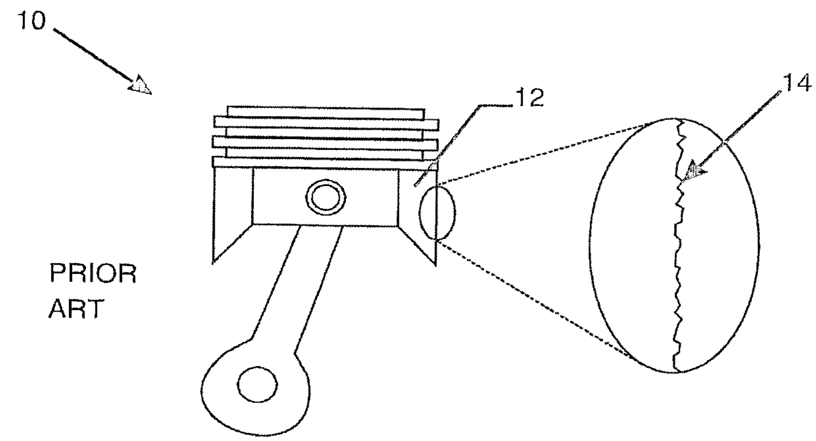


Fig. 1

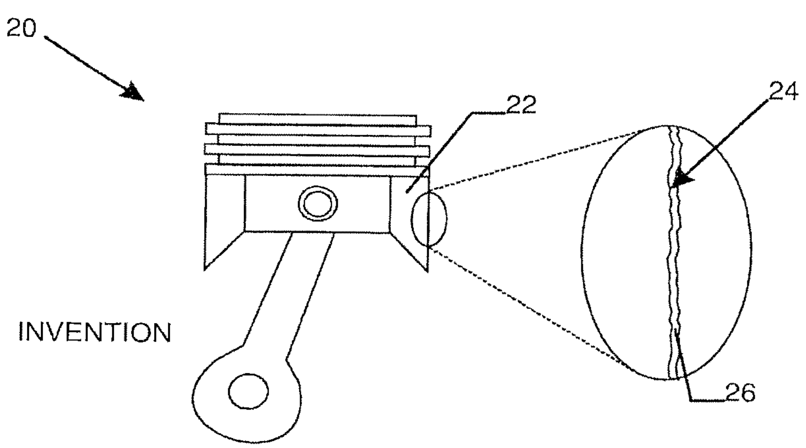


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050340

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 F02F3/10 F02B77/02 F16J1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 F02F F02B F16J F01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 14, 5 March 2001 (2001-03-05) & JP 2000 320670 A (KAYABA IND CO LTD), 24 November 2000 (2000-11-24)	1,4,5
Y	abstract; figure	7,8,11
Y	WO 97/14555 A (ADVANCED REFRACTORY TECH) 24 April 1997 (1997-04-24)	7,8,11
A	page 3, line 15 -page 11, line 6 page 21, line 4 -page 23, line 27; figures 2-6	1,4,6,9, 10
A	US 5 249 554 A (GANGOPADHYAY ARUP K ET AL) 5 October 1993 (1993-10-05) page 2, line 23-32; figures column 3, line 48 -column 9, line 43	1,4,5, 8-10

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 August 2004	30/08/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Luta, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050340

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 198 25 860 A (ELGAN DIAMANTWERKZEUGE GMBH &) 16 December 1999 (1999-12-16) column 3, line 61 -column 6, line 68 ---	2,3,9,10
A	US 4 666 786 A (KATO SHINJI ET AL) 19 May 1987 (1987-05-19) abstract -----	4,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2004/050340

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WO 9714555	A	24-04-1997	AU	7371496	A	07-05-1997
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			DE	69316575	T2	14-05-1998
			EP	0605992	A1	13-07-1994
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			JP	5083636	B	26-11-1993
			JP	60197880	A	07-10-1985
			DE	3503859	A1	19-09-1985

Appendix B

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) **Title:** A LAYERED STRUCTURE

(57) **Abstract:** The invention relates to a layered structure comprising a first intermediate layer, said first intermediate layer comprising at least one element of group IVB, group VB or group VIB; a second intermediate layer deposited on top of said first intermediate layer, said second intermediate layer comprising a diamond-like nanocomposite composition; a diamond-like carbon layer deposited on top of said second intermediate layer. The invention further relates to the use of a substrate coated with such a layered structure for high shear and/or high impact applications and to a method to cover a substrate with such a layered structure.

A LAYERED STRUCTURE

Field of the invention.

The invention relates to a layered structure comprising a first intermediate layer comprising at least one element of group IVB, VB or IVB, a second intermediate layer comprising a diamond-like nanocomposite composition and a diamond-like carbon layer.
The invention further relates to a substrate covered at least partially with such a layered structure and to a method to cover a substrate with such a layered structure.

Background of the invention.

It is generally known to coat substrates with a diamond-like carbon coating (DLC). DLC coatings are amorphous hydrogenated carbon films (a-C:H) characterised by a high hardness, a low coefficient of friction and excellent wear resistance.
However, because of the high compressive residual stresses in the coating, the adhesion of DLC coatings to the substrate is often too poor. This is an important drawback of DLC coatings, limiting the use of DLC coatings for certain applications.

Many attempts have been made to improve the adhesion of a DLC coating to the substrate for example by using an intermediate layer between the substrate and the DLC coating.
An example of such an attempt comprises the use of a diamond-like nanocomposite (DLN) layer as intermediate layer between the substrate and the DLC layer as described in WO 98/33948.
Diamond-like nanocomposite coatings comprise C, H, O and Si. Generally, DLN coatings comprise two interpenetrating networks a-C:H and a-S:O. DLN coating are commercially known as Dylyn® coatings.

Also the use of a titanium or a titanium-based intermediate layer between the substrate and a DLC layer is known in the art to improve the adhesion of a DLC coating to a substrate.
For this type of layered structures a gradual change from a titanium or titanium-based layer to a DLC layer is required.

Therefore, first a titanium or a titanium-based layer is deposited on a substrate by means of a PVD process, subsequently DLC is deposited on the titanium or titanium-based layer. The composition of the titanium or titanium-based layer is thereby gradually changed from a titanium or titanium-based layer to a DLC layer.
However, a serious problem of the use of titanium or titanium-based interlayers is the target poisoning of the titanium target. Because of this target poisoning, the transition between the titanium or titanium-based layer and the DLC layer is not reproducible.

Another disadvantage of the application of a layered structure of a titanium or titanium-based layer and a DLC coating is the poor corrosion protection that is obtained.
This is the consequence of the bad surface coverage (line-of-sight locations) on for example the backside surfaces of a substrate to be coated. These surfaces are not exposed to the beam of titanium atoms.

Summary of the invention.

It is an object of the present invention to provide a layered structure comprising a DLC coating having an improved adhesion to a substrate.
It is another object of the invention to provide a layered structure that may withstand a high load and that is thus suitable for high impact and high shear applications.
It is a further object to provide a substrate covered with a structure having an improved surface coverage.

According to a first aspect of the invention, a layered structure is provided.
The layered structure according to the present invention comprises

- a first intermediate layer, comprising at least one element of group IVB, VB or VIB;
- a second intermediate layer deposited on the first intermediate layer, the second intermediate layer comprising a diamond-like nanocomposite composition;

- a diamond-like carbon layer, deposited on said second intermediate layer.

The first intermediate layer

The first intermediate layer comprises at least one element of the group IVB, VB or VIb.
Preferably, the first intermediate layer comprises titanium and/or chromium as for example a titanium layer, a chromium layer, a titanium-based layer or a chromium-based layer.
A titanium-based layer may for example comprise a TiC layer, a TiN layer or a TiCN layer. A chromium-based layer may for example comprise a CrN layer or a Cr_3C_2 layer.
For many applications a titanium-based layer is preferred to a chromium-base layer as it is easier to rework or refurbish layered structures comprising a titanium-based layer.
For example, a reactive ion etching used to decoat will not work with a chromium-based interlayer.

The thickness of the first intermediate layer is preferably between 0.001 and 1 μm. More preferably, the thickness of the first intermediate layer is between 0.1 and 0.5 μm.

The first intermediate layer may be deposited by any technique known in the art. Preferred techniques comprises physical vapor deposition techniques as sputtering or evaporating.

The second intermediate layer

The second intermediate layer comprises a diamond-like nanocomposite composition.
A diamond-like nanocomposite composition comprises an amorphous structure of C, H, Si and O.
Preferably, the nanocomposite composition comprises in proportion to the sum of C, Si, and O : 40 to 90 %C, 5 to 40 % Si, and 5 to 25 % O (expressed in at%).

Preferably, the diamond-like nanocomposite composition comprises two interpenetrating networks of a-C:H and a-Si:O.

The diamond-like nanocomposite coating may further be doped with a metal, such as a transition metal of Group IV to VII. The coating can be doped to influence the conductivity of the coating. W, Zr and Ti are for example well suited as doping element.

The second intermediate layer has a thickness which is preferably between 0.01 and 5 μm. More preferably, the thickness is beween 0.1 and 1 μm, for example between 0.2 and 0.5 μm.

The second intermediate layer may be deposited by any technique known in the art. A preferred technique comprises chemical vapor deposition (CVD), such as plasma assisted chemical vapor deposition (PACVD).

<u>Diamond-like carbon coating</u>

The diamond-like carbon coating comprises amorphous hydrogenated carbon (a-C:H).
Preferably, a diamond-like carbon coating comprises a mixture of sp^2 and sp^3 bonded carbon with a hydrogen concentration between 0 and 60 at%.

The DLC coating may be metal doped, for example to influence the electrical conductivity of the coating. Preferred doping elements are transition metals of Group IV to VII such as W, Zr and Ti.

The thickness of the DLC coating is preferably between 0.1 and 10 μm.

The DLC coating may be deposited by any technique known in the art. A preferred technique comprises chemical vapor deposition (CVD), such as plasma assisted chemical vapor deposition (PACVD).

Although the applicant does not want to be bound to any theory, it is believed that the gradation of the hardness of the layers is important to obtain the good results of a layered structure according to the present invention.
In the case a titanium layer is used as intermediate layer for a DLC coating, there is a soft substrate with a layer of soft Ti. DLC deposited on such a stack is prone to puncturing.
In the layered structure according to the present invention comprising a first intermediate layer and a second intermediate layer comprising DLN, the second intermediate layer provides extra support. Furthermore, the second intermediate layer, having a hardness in between the hardness of the first intermediate layer and the hardness of the DLC coating, provides a cushioning effect.

Possibly, the layered structure according to the present invention further comprises one or more additional layers as for example a layer comprising a diamond-like nanocomposite composition on top of the diamond-like carbon layer.
In another embodiment, the layered structure further comprises a diamond-like nanocomposite layer on top of the diamond-like carbon layer and a diamond-like carbon layer on top of the diamond-like nanocomposite layer.
It is clear for a person skilled in the art that the number of the additional layers can be varied according to the desired properties of the layered structure.

The top layer of the layered structure can be chosen depending on the desired properties of the layered structure and depending on the application.
When a DLC layer is deposited on top of the layered structure, the hardness and low-wear characteristics, typical for a DLC type coating prevail. This implies that by depositing a DLC layer on top of the layered structure a high wear and abrasion resistance coating is

obtained. Thicknesses higher than these of conventional DLC coatings can be deposited in this way.
In the case a DLN coating is deposited as top layer, the layered structure is characterized by a low surface energy and by a low friction coefficient. Such a layered structure is in particular suitable as non-sticking coating.

According to a second aspect of the invention, a substrate covered at least partially with a layered structure as described above is provided.

A great advantage of the layered structure according to the present invention is the high corrosion protection that may be obtained because of the good surface coverage.
The surfaces of the substrate that are not coated or not coated well with the first intermediate coating because they are not exposed to the beam of atom(s) of group IVB, group VB or group VIB will be protected by the second intermediate layer and the diamond-like carbon layer.

According to a third aspect of the invention, the use of a substrate covered at least partially with a layered structure as described above for high impact and/or high shear applications is provided.
The substrate according to the present invention can be used for high impact and/or high shear applications because of the strong adhesion of the DLC coating to the substrate by means of the first and second intermediate layer.
The layered structure according to the present invention is for example suitable as coating for components for metal forming applications such as staking tools, punches, mandrels, necking dies for example used for aluminium can making.
The layered structure according to the invention is also suitable as coating for parts used for semiconductor chip manufacturing, metrology, lithography or testing equipment such as electrostatic chucks, wafer handlers, lift pins, precision alignment components, punches and tools used in electronic packaging and components used for wafer probing.

Furthermore the layered structure can be used as coating for blow molding components and components for textile machinery such as thread splits, bases, pins and cores; for engine components (as for example racing components) such as lifters, tappets, connecting rods and wrist pins; for neck rings used for plastic preforms.
Additionally, the layered structure according to the present invention is suitable for the protection of copper and nickel based alloys.

According to a further aspect of the invention, a method to cover a substrate with a layered structure is provided.
The method comprises the steps of

- providing a substrate;
- applying a first intermediate layer, said first intermediate layer comprising at least one element of group IVB, group VB or group VIB, such as titanium and/or chromium;
- applying a second intermediate layer, said second intermediate layer comprising a diamond-like nanocomposite composition;
- applying a diamond-like carbon layer.

If desired, the deposition of the first intermediate layer may be completely stopped before the application of the second intermediate layer. In this way a reproducible transition between the layers can be obtained.

Description of the preferred embodiments of the invention.

The characteristics of three different coating types are compared. The coating types are deposited on a hardened steel substrate.
The three coating types are subjected to a Rockwell adhesion test and to a scratch adhesion test.

a) The first coating type comprises a layered structure of a DLN layer and a DLC layer deposited on top of this DLC layer;
b) The second coating type comprises a layered structure of a titanium layer and a DLC layer deposited on top of this titanium

layer. The composition of the titanium layer is gradually changed from a titanium layer to a DLC layer.

c) The third coating type comprises a layered structure according to the present invention. This layered structure comprises a titanium layer, a DLN layer deposited on top of the titanium layer and a DLC layer deposited on top of the DLN layer. There is no gradient between the titanium and the DLN layer, whereas the DLN layer is gradually changing to a DLC layer.

The adhesion of the second and third coating type measured by means of the Rockwell C indentation test is better than the adhesion of the first coating type.
The HF value for the first coating type is HF 3-5. For the second coating type a HF value 1-3 is measured, whereas for the third coating type a HF value 1-3 is measured.

The critical load to obtain delamination in a scratch adhesion test is for the third coating type between 22 and 35 N. For the first coating type a critical load between 15 and 30 N is obtained; for the second coating type a critical load between 15 and 27 N is obtained.
Comparison of the scratch adhesion of the different coatings indicates that the third coating type gives the best Lc_2-values.

A coating of the first type does not perform well in high shear and high impact loading applications.
A coating of the second type performs slightly better under high impact loading. However, under high shear loading there is possibility of wear and coating removal.
A coating of the third type performs very well under both high impact and high shear applications.

A coating of the second type and a coating of the third type are compared in a high impact aluminum sheet metal forming application. The coating of the third type provides an increased life time. Compared

to the life time of a coating of the second time the life time of a coating of the third type is 3 to 4 times longer.

CLAIMS

1. A layered structure comprising
   - a first intermediate layer, said first intermediate layer comprising at least one element of group IVB, group VB or group VIB;
   - a second intermediate layer deposited on top of said first intermediate layer, said second intermediate layer comprising a diamond-like nanocomposite composition;
   - a diamond-like carbon layer deposited on top of said second intermediate layer.

2. A layered structure according to claim 1, whereby said first intermediate layer comprises titanium and/or chromium.

3. A layered structure according to claim 1 or 2, whereby said structure further comprises at least a layer comprising a diamond-like nanocomposite composition on top of said diamond-like carbon layer.

4. A layered structure according to any one of the preceding claims, whereby said first intermediate layer has a thickness between 0.001 and 1 μm.

5. A layered structure according to any one of the preceding claims, whereby said second intermediate layer has a thickness of 0.01 to 5 μm.

6. A layered structure according to any one of the preceding claims, whereby said diamond-like carbon layer has a thickness between 0.1 and 10 μm.

7. A layered structure according to any one of the preceding claims, whereby said nanocomposite composition comprises in

proportion to the sum of C, Si, and O in at% 40 to 90 % C, 5 to 40 % Si, and 5 to 25 % O.

8. A layered structure according to any one of the preceding claims, whereby said second intermediate layer comprises a metal doped diamond-like nanocomposite composition.

9. A layered structure according to any one of the preceding claims, whereby said diamond-like carbon layer is doped with a metal.

10. A substrate covered at least partially with a layered structure according to any one of claims 1 to 9.

11. The use of a substrate according to claim 10 for high shear and/or high impact applications.

12. A method to cover a substrate with a layered structure according to any one of claims 1 to 10, whereby said method comprises the steps of

- providing a substrate;
- applying a first intermediate layer, said first intermediate layer comprising at least one element of group IVB, group VB or group VIB;
- applying a second intermediate layer, said second intermediate layer comprising a diamond-like nanocomposite composition;
- applying a diamond-like carbon layer.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C14/14 C23C24/02 C23C14/06 C23C16/02 C23C28/00
F16C33/12 F16C33/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C F16C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ovejero, E

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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